Linking groundwater age and chemistry data to determine redox reaction rates and trends in nitrate concentrations in agricultural areas of the United States.

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Use of industrially fixed nitrogen (N) fertilizer for agricultural purposes has increased more than 20 fold in the United States (U.S.) and more than 45 fold globally since 1945. As a result, there has been growing concern about the consequences of increases in the amounts of anthropogenic N circulating in the atmosphere, hydrosphere, and biosphere. The U.S. Geological Survey's National Water-Quality Assessment Program has collected groundwater samples along flow paths in more than 20 agricultural areas covering a range in hydrogeologic settings to evaluate the trends and transformations of agricultural chemicals. Historical trends in nitrogen fluxes to groundwater were evaluated by relating the recharge dates of groundwater samples, estimated using tracer (e.g., chlorofluorocarbon) concentrations, with concentrations of the parent compound at the time of recharge, estimated by summing the molar concentrations of the parent compound and its transformation products in the age-dated sample. Results from this analysis indicate that median nitrate (NO_3^-) recharge concentrations have increased markedly over the last 50 years: increasing from 4 mg/L (as N) in samples collected prior to 1983 to 7.5 mg/L (as N) in samples collected since 1983. Trends in nitrate concentrations in recharging groundwater were related to increases in the amount of fertilizer applied. Estimates of the portion of applied N reaching the water table ranged from 4 to 49% among the sites, with a median value of 14%.

The fate of NO_3^- and many other groundwater contaminants is dependent on aquifer redox conditions. The reduction of oxygen is the most energetically favorable reaction that microorganisms use to oxidize organic material or other electron donors (e.g., pyrite). As a result, other reduction reactions (e.g., denitrification) affecting contaminant transport typically do not occur until most dissolved oxygen (DO) has been consumed. To improve assessments of contaminant transformations, first-order oxygen reduction rates were determined in each of 20 study areas by relating measured DO concentrations to groundwater age. First-order rate constants for these aquifers ranged from 0.03 to 0.18 yr^{-1} and were only weakly correlated with recharge temperature. DO reduction rates varied markedly within some sites, likely the result of changes in the supply of electron donors. The range in oxygen reduction rates both within and between sites is an important consideration when assessing the transport of redox-active contaminants.